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| 13. ABSTRACT (Maximum 200 words)<br>The fluid dynamics in a vertical reactor for high pressure vapor transport (HPVT) of compound semiconductors is modeled. The modeling is for the growth of II-IV-V <sub>2</sub> chalcopyrite ZnGeP <sub>2</sub> and addresses the flow of dense phosphorus gas at 3.42x10 <sup>5</sup> Pascals pressure. Effects of density variations on p-polarized reflectance spectroscopy are also examined. The mathematical model for transport processes is described by the full gasdynamic equations (Navier Stokes equations coupled with an equation for energy). In addition, buoyancy effects are included in the model through the gravitational term in the momentum equation. Numerical results of a 3-D steady flow are presented using a finite element discretization with non-uniform, quadrilateral elements. The numerical simulations were performed to study the effects of gravitational-induced buoyancy-driven convection flows in HPVT crystal growth. |  |   |   |   |
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Report prepared by

H.T. Banks

April 25, 1995

GRANT AMENDMENT  
UNITED STATES AIR FORCE  
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
BUILDING 410, BOLLING AFB, D. C. 20332-6448

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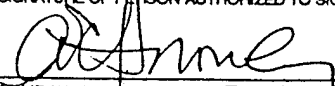
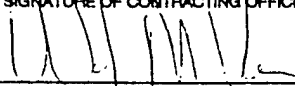
THE GRANT IDENTIFICATION ABOVE IS MODIFIED AS FOLLOWS:

By changing the duration from 1 to 5.5 months and establishing an expiration date of 28 Feb 95.

The final reporting requirements are revised as shown below and shall be submitted on the dates and in the quantities shown below:

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EXCEPT AS PROVIDED WHEREIN, ALL TERMS AND CONDITIONS OF THE GRANT, AS HERETOFORE CHANGED, REMAIN UNCHANGED AND IN FULL FORCE AND EFFECT.

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| NAME AND TITLE OF SIGNER (Type or Print)<br>Dr. Charles E. Knowles<br>Coordinator Centers<br>Institutes and Laboratories     |  | NAME OF CONTRACTING OFFICER (Type or Print)<br>WENDY M. VEON<br>Administrative Contracting Officer                       |  |
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## Research Activity Summary

This grant was initially for one month (Oct. 15-Nov. 14, 1994) with the expectation of a 12 month additional funding period. The additional 12 month funding was delayed and a no-cost extension was granted to permit the effort to continue.

In spite of a shortfall in funding, substantial progress on the initial phase of this work was achieved. Several postdoctoral associates were hired and training began. Three papers (the abstracts are appended as part of this report) were produced by February, 1995.

We have made an excellent start and anticipate we will be able to achieve the original proposed research goals if the additional 12 month funding is forthcoming.

# Heteroepitaxy of Lattice-Matched Compound Semiconductors on Silicon

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## Abstract

The heteroepitaxial overgrowth of silicon by nearly lattice matched compound semiconductors is reviewed in the context of the separation of the chemical problems associated with the initial sealing of the silicon surface by a contiguous epitaxial compound film from the problems associated with the generation of strain during heteroepitaxial growth. Of the mixed compound systems available dilute solid solutions of composition  $\text{Al}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$  and  $\text{ZnS}_y\text{Se}_{1-y}$  as well as  $\text{ZnSi}_x\text{Ge}_{1-x}\text{P}$  are suitable candidates for the exactly lattice-matched epitaxial overgrowth of silicon. Real-time process monitoring by non-intrusive methods is important for gaining an understanding of the epitaxial overgrowth mechanism and for controlling the film properties. A new method, p-polarized reflectance spectroscopy (PRS) is introduced that provides detailed information about the growth rate per cycle, the bulk optical properties of the film and its topography. Sub-monolayer resolution is accomplished for thousands of Å of film growth by pulsed chemical beam epitaxy (PCBE). While the cubic materials choices considered here generally afford easier control of the electrical and optical properties, the non-cubic materials have advantages in the sealing of the silicon surface because of their anisotropic growth and the formation of metastable solid solutions that may permit the graded growth of compound films under exactly lattice-matched conditions. Therefore, no clear cut preference in the materials selection for nearly lattice-matched overgrowth of silicon by compound semiconductors can be identified at this time.

## HIGH PRESSURE VAPOR TRANSPORT OF $\text{ZnGeP}_2$ : I. PARAMETER EVALUATION

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### Abstract

$\text{ZnGeP}_2$  crystals and epilayers can be grown by chemical vapor transport using phosphorus or hydrogen chloride as transporting agent. The limiting factor in the transport rate is the volatility of germanium which has a seven order of magnitude smaller partial pressure than elemental zinc. Excluding oxygen using carbon films inside the growth vessels and employing a nitrogen shroud in the furnace tube also transport of  $\text{ZnGeP}_2$  will be obtained when phosphorus is used as transport agent. Optical absorption measurements above show the presence of absorption band head systems which cannot be explained by the absorption lines of  $\text{P}_2$ ,  $\text{P}_4$ ,  $\text{PO}$  or  $\text{GeO}$ . These new bands are also present in the vapor above  $\text{ZnGeP}_2$  but not above  $\text{ZnP}_2$ . The experimental findings have been simulated by thermochemical calculations taking into account estimated values for the vapor species  $\text{GeP}$ .

### I. Introduction

$\text{ZnGeP}_2$  crystallizes in the chalcopyrite structure which can be inferred from the zincblende lattice by doubling the unit cell of  $\text{ZnS}$  and ordering the cation sublattice. In the tetragonal unit cell a small distortion occurs in the direction of the c-axis which substantially affects the optical properties of this compound semiconductor. The material is of interest in context of its non-linear optical properties and can be applied as optical parametric oscillator or for frequency mixing. For this reason, thick films or crystals of high transparency are in demand, which can be grown from the vapor phase.

The dissociation pressure of the ternary chalcopyrite  $\text{ZnGeP}_2$  amounts to 3.5 bars at the melting point at 1295 K [2]. In the last contribution to this conference series [1] we directed attention to the sensitive change of this equilibrium pressure with composition of the condensed phase. Therefore, close control of the partial pressures of the constituting elements and their gaseous compounds during vapor growth is necessary.

In this paper we discuss vapor phase transport experiments of  $\text{ZnGeP}_2$  in oxygen free environment using phosphorus or hydrogen chloride as transport agent. It is assumed that germanium as well as zinc could form volatile phosphorus species. To detect new phosphorus bearing gas species, optical absorption spectroscopy of the vapor phases over  $\text{ZnGeP}_2$ ,  $\text{ZnP}_2$  and  $\text{GeP}$  has been performed. The results are compared with thermochemical calculations using the free energy minimization method described by Ericson [3].

### II. Transport Experiments

In order to distinguish the conditions of multiphase from those for single phase transport under exclusion of deleterious effects of residual oxygen contamination of the vapor atmosphere experiments

# HIGH PRESSURE VAPOR TRANSPORT OF $\text{ZnGeP}_2$ :

## II. THREE-DIMENSIONAL SIMULATION OF GASDYNAMICS UNDER MICROGRAVITY CONDITIONS <sup>1 2</sup>

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### Abstract

The fluid dynamics in a vertical reactor for high pressure vapor transport (HPVT) of compound semiconductors is modeled. The modeling is for the growth of II-IV-V<sub>2</sub> chalcopyrite  $\text{ZnGeP}_2$  and addresses the flow of dense phosphorus gas at  $3.42 \times 10^5$  Pascals pressure. Effects of density variations on p-polarized reflectance spectroscopy are also examined. The mathematical model for transport processes is described by the full gasdynamic equations (Navier Stokes equations coupled with an equation for energy). In addition, buoyancy effects are included in the model through the gravitational term in the momentum equation. Numerical results of a 3-D steady flow are presented using a finite element discretization with non-uniform, quadrilateral elements. The numerical simulations were performed to study the effects of gravitational-induced buoyancy-driven convection flows in HPVT crystal growth.

### Introduction

Non-linear optical interactions in birefringent materials find applications in phase-matched harmonic generation and frequency mixing. In particular,  $\text{ZnGeP}_2$ , which has a high non-linear susceptibility coefficient, has been used for manu-